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THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS. THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

AN EXPANSION OF A DISSERTATION SUBMITTED
TO THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By
FRANK REA MAYO

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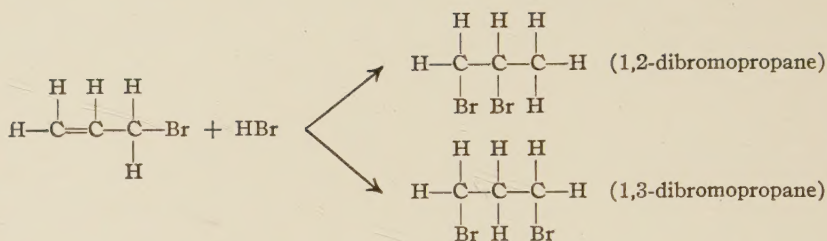
THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS. THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

Introduction

The theory of partial polarity of the ethylene bond proposed by Kharasch¹ postulates that in unsymmetrical ethylene compounds, one of the two electron pairs constituting the double bond is held in common by the two carbon atoms concerned and the other behaves as if it were decidedly closer to one of the carbon atoms than to the other. It is an essential part of the theory also that this second electron pair lies closer in general to that carbon atom which carries the least electronegative radicals. In view of some discrepancies between the predicted and the experimentally recorded results, it became necessary to repeat the work on the addition of hydrogen bromide to allyl bromide and many other unsaturated compounds. In the course of this work, the effect of peroxides on the direction of addition was discovered. This paper deals with the magnitude of that effect on the addition of hydrogen bromide to allyl bromide, but observations made on other systems show clearly that the results obtained in the case under discussion have a wide applicability, the limits of which have not yet been determined.

Hydrogen bromide may add to allyl bromide in two different ways

(1) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).



Both reactions have been noted many times and a copious literature exists on the various physical and chemical influences which may cause the addition to proceed in one way or the other.² In the light of our findings, all of these results need reinterpretation, for seldom were any of the workers evaluating one factor at a time.

Obviously, no discussion of the results of an addition of hydrogen bromide to allyl bromide can be of much significance unless there exists a fairly satisfactory method for the quantitative analysis of the resulting mixture. We have found the analytical methods in existence unsatisfactory and have evolved a method which enables us to determine the percentage composition of a mixture of the two dibromides concerned with a precision of five per cent. The analytical methods employed, the technique of addition under definitely controlled conditions, as well as the demonstration that no rearrangement of allyl bromide or the addition products occurs during the addition, are described in the experimental part.

Factors Influencing the Addition of Hydrogen Bromide to Allyl Bromide

1. **The Peroxide Effect.**³—The following observations convinced us that there were still unsuspected factors which influenced the addition under investigation. If the addition is carried out *in vacuo*,⁴ different samples of allyl bromide reacted with varying velocities to give different proportions of addition products (Table I). In the majority of these runs, the product of the addition was 65–85% 1,2-dibromopropane and an

(2) Geromont, *Ann.*, **150**, 369 (1871); Reboul, *Compt. rend.*, **74**, 614 (1872); **76**, 1270 (1873); Lermontoff, *Ann.*, **182**, 358 (1876); Bogomolez, *Ber.*, **11**, 1257 (1878); *Bull. soc. chim.*, [2] **30**, 23 (1878); Reboul, *Ann. chim.*, [5] **14**, 470 (1878); Erlenmeyer, *Ann.*, **197**, 169 (1879); Roth, *Ber.*, **14**, 1351 (1881); Niederist, *Monatsh.*, **3**, 838 (1882); Bruylants, *Rec. trav. chim.*, **28**, 246 (1909); Böeseken, *ibid.*, **34**, 99 (1915); **37**, 260 (1918); Holleman and Matthes, *Proc. Acad. Sci. Amsterdam*, **21**, 90 (1918); Frankel and Kuk, *Biochem. Z.*, **226**, 223 (1930); Clark and Gray, *Trans. Roy. Soc. Can.*, [3] **24**, Sect. 3, 111 (1930); Wibaut, *Rec. trav. chim.*, **50**, 313 (1931).

(3) All of the experiments of which the results are reported in this section were made in the dark at room temperature in the absence of solvents.

(4) In these papers, the expression *in vacuo* will indicate that while the reaction mixtures were frozen solid at the temperature of liquid air, residual gases in the bomb tubes were removed by evacuation before the tubes were sealed off. Naturally there was no vacuum, but pressure, in the tubes when the reaction mixtures warmed up. For further details, consult the experimental part.

average of 88% of the allyl bromide reacted in ten days.⁵ Reaction occurred much more rapidly in the remaining runs in which 1,3-dibromopropane was the principal product. That this variation in both yield and product was due to some sort of oxygen or peroxide effect is indicated by a consideration of the results of Table II. As long as the reaction was run in the presence of air or oxygen, as many as fifteen samples of allyl bromide reacted alike and yielded almost entirely ($87 \pm 5\%$) 1,3-dibromopropane in a comparatively rapid reaction. In at least one of these runs (No. 172) the addition was complete within an hour.

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE DARK AT ROOM TEMPERATURE IN THE ABSENCE OF SOLVENTS AND GASES^a

No.	Yield, %	Reaction time	% 1,3- ^b	Remarks
135	86	9 days	32	
160	94	11 days	33	
161	95	11 days	29	
181	99	18 days	87	1.25 moles HBr used
182	100	8 days	17	3.03 moles HBr used
185	100	10 days	83	
198	100	10 days	71	
205	91	10 days	18	
208	85	15 days	28	1.21 moles HBr used
212	88	9 days	27	Dried 3 hours with large excess P_2O_5
214	91	9 days	24	Dried 15 min. with small amount P_2O_5
233	87	10 days	29	Dried 4.5 hours
234	87	10 days	22	Dried 15 min.
258	85	9 days	26	
259	83	9 days	25	
277	96	9 days	46	
278	87	9 days	18	
350	100	12 days	76	
361	79	10 days	26	
443	82	10 days	42	
362	75	10 days	13	Nitrogen passed through allyl bromide for ten minutes before solution of hydrogen bromide
363	100	10 days	74	Same, but with oxygen instead of nitrogen
137	78	9 days	17	Dried with Na_2SO_4 instead of P_2O_5
156	91	10 days	24	Dried with Na_2SO_4 instead of P_2O_5
164	93	10 days	33	Dried with Na_2SO_4 instead of P_2O_5
165	100	10 days	71	Dried with Na_2SO_4 instead of P_2O_5
184	96	10 days	46	Dried with Na_2SO_4 instead of P_2O_5
204	98	10 days	15	Dried with Na_2SO_4 instead of P_2O_5
407	76	9 days	13	Dried with $CaCl_2$ instead of P_2O_5
191	100	3 days	84	Dried with silica gel ^c instead of P_2O_5
203	100	6 days	85	Dried with silica gel ^c instead of P_2O_5

(5) It has been our experience that under peroxide-free conditions, the normal addition proceeds to the extent of about 35% the first day, 15% the second day, and more slowly thereafter so that a yield of 85-90% is obtained in ten days.

TABLE I (Concluded)

No.	Yield, %	Reaction time	% 1,3- ^b	Remarks
386	85	11 days	11	0.011 mole hydroquinone present
387	97	11 days	11	.014 mole diphenylamine present
428	93	9 days	11	.014 mole mercaptobenzothiazole present
442	98	10 days	10	.029 mole thiocresol present
445	89	65 hours	10	.058 mole tertiary butyl isocyanide present
200	76	4 days	24	Reaction mixture distilled <i>in vacuo</i> without drying
207	87	9 days	18	
232	100	10 days	71	
222	92	10 days	20	Reaction mixture was not dried or distilled, but bomb tube was evacuated before sealing
243	98	12 days	66	
245	99	9 days	83	
242	99	12 days	84	
285	92	15 months	26	Saturated 11 times with HBr at -10° , but not dried, distilled or evacuated

^a Except as otherwise noted, these reaction mixtures were prepared according to the drying and distillation procedure described in the experimental part, and 1.5 moles of hydrogen bromide was used.

^b The figures given in this column represent the percentage of 1,3-dibromopropane in the pure addition product. The remainder of the product is 1,2-dibromopropane.

^c The large yields of 1,3-dibromopropane obtained with this drying agent are probably accounted for by the fact that the silica gel was not degassed before it was used.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF AIR OR OXYGEN^a

No.	Yield, %	Reaction time	% 1,3- ^b	Remarks
X10	99	5 days	90	Mean of three results
B2	100	5 days	92	Mean of two results
172	100	1 hour	90	
219	99	20 hours	90	Mean of two results
244	100	9 days	88	(V) ^a undried air admitted, mean of two results
415	100	18 hours	82	(V) ^a dried air admitted
251	100	5 days	84	(V) ^a dried oxygen admitted, mean of four results
369	87	8 days	10	0.01 mole hydroquinone added
382	60	2 days	11	.01 mole resorcinol added
374	98	9 days	11	.014 mole diphenylamine added, mean of two results
431	96	9 days	16	.011 mole phenyl- β -naphthylamine added
435	93	9 days	11	.012 mole dimethylaniline added
373	100	16 hours	89	.02 mole KCN added
439	100	20 hours	89	.025 mole NH_4Br added
441	100	21 hours	89	.014 mole diphenyl ether added

^a Except as otherwise noted, in these runs the solutions of hydrogen bromide in allyl bromide were sealed off in bomb tubes containing air at -75° , without any drying or distillation. (V) indicates that the reaction mixtures were dried and distilled and that then air was admitted as described in the experimental part. 1.5 moles of hydrogen bromide was used in all runs.

^b See corresponding note to Table I.

A simple adaptation of the thiocyanate test showed that various samples of allyl bromide differed widely in their ability to oxidize ferrous ion. Colors ranging all the way from the faintest pink to a deep red were developed in the thiocyanate solution. Furthermore, our experience with additions *in vacuo* indicated that the amount of 1,3-dibromopropane formed was within wide limits roughly proportional to the oxidizing power of the allyl bromide. We have assumed that this oxidizing power is due to the "peroxide content" of the allyl bromide, although we have not isolated as yet in pure form any such compound as allyl bromide peroxide. Nevertheless, we feel justified in the assumption because an addition reaction run *in vacuo* with allyl bromide of little or no oxidizing power, but where 0.02 mole of benzoyl peroxide was added to the reaction mixture (Table III) yielded exactly the same product as if allyl bromide of high oxidizing power had been employed.

TABLE III

THE EFFECT OF SOME OXIDIZING AGENTS ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE ABSENCE OF AIR^a

No.	Oxidizing agent	Mole of ox. agent	Yield, %	Reaction time	% 1,3- ^b	Remarks
335	Benzoyl peroxide	0.023	95	18 hours	82	
364	Bromine	.004	79	9 days	24	Mean of two results
366	Lead dioxide	.005	26	18 hours	15	

^{a,b} See corresponding notes to Table I.

Allyl bromide is quite sensitive to oxidation by atmospheric oxygen. The pure substance has been found to give a very strong peroxide test after standing in the dark at room temperature for two months. Furthermore, while a sample of peroxide-free allyl bromide gives over 80% of 1,2-dibromopropane *in vacuo*, the same sample under identical experimental conditions will give over 70% of the 1,3 isomer if oxygen is bubbled through it for ten minutes before the addition of the hydrogen bromide (Table I, No. 363). It can also be demonstrated that the oxidizing power of the sample was increased by the ten-minute treatment with oxygen. *In our opinion, therefore, unless conditions are attained which eliminate this oxygen or peroxide effect, no statement as to the direction of addition of hydrogen bromide to a sample of allyl bromide, the peroxide content of which is unknown, is of significance.*

Clearly two alternative methods present themselves for obtaining consistently only one product in the addition of hydrogen bromide to allyl bromide. The first is to attain conditions where all the samples of allyl bromide react as if they contained large quantities of peroxide; the second is to attain conditions where all samples of allyl bromide react as if they contained no peroxides at all. Since allyl bromide is very sensitive to oxidation, the first condition is easily attained by running

the reaction in the presence of air. That this air effect is due to oxygen and not to the presence of some other gas besides hydrogen bromide is shown by the fact that when the reaction is run in the presence of an inert gas such as hydrogen, nitrogen, nitric oxide or nitrogen dioxide (Table IV), the result is exactly the same for any particular sample as if the run had been made *in vacuo*.

TABLE IV

THE EFFECT OF FOREIGN GASES OTHER THAN OXYGEN ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

All of these runs were prepared according to the usual vacuum drying and distillation technique. Gases were then admitted through a long tube containing phosphorus pentoxide, as shown in Fig. 3. 1.50 moles of hydrogen bromide was used in all expts.

No.	Yield, %	Reaction, time	% 1.3 ^b	Remarks
Commercial electrolytic hydrogen admitted				
250	90	8 days	49	No special treatment of hydrogen
286	100	9 days	83	Hydrogen passed through alkaline potassium permanganate, concd. sulfuric acid, and silica gel
291	98	9 days	50	
292	100	9 days	84	
302	84	10 days	26	Same treatment, with tower of alkaline sodium hydro-sulfite added to train
303	86	10 days	40	
429	77	10 days	20	Hydrogen passed through tube of hot copper prepared by reduction of granulated copper oxide
Commercial nitrogen admitted				
287	83	9 days	26	No special treatment of nitrogen
Nitric oxide from sodium nitrite and acid ferrous sulfate solutions admitted				
372	92	9 days	11	Nitrogen passed through allyl bromide for 12 min. before solution of hydrogen bromide. 0.01 mole of hydroquinone present with P ₂ O ₅ during drying
Nitrogen dioxide from copper and concentrated nitric acid admitted				
392	94	7 days	17	No special treatment of oxide

^b See corresponding note to Table I.

The second condition is attained with almost equal ease by the addition of an antioxidant to the reaction mixture. A wide variety of antioxidants have been used, some neutral, some basic, and some acidic. All of them affect the course of the reaction in an almost identical manner. If the antioxidant is present in sufficient quantity, the addition product, irrespective of the peroxide content of the allyl bromide or the presence or absence of oxygen, is almost entirely 1,2-dibromopropane (Tables I and II).

An explanation is perhaps due here as to our use of the word "antioxidant." That oxygen is responsible for the formation of 1,3-dibromopropane in the dark has been amply demonstrated by many experiments. Whether the materials which we call antioxidants act in the capacity of merely breaking a chain reaction, or by inactivating the double bond and

decreasing the oxygen effect, or whether they effectively decompose peroxides under the experimental conditions, or remove oxygen is difficult to state on the basis of available information. We are rather inclined, from a consideration of Table V, to believe that the materials actually remove or decompose the peroxides in the allyl bromide, but only under the experimental conditions of the addition of hydrogen bromide.

TABLE V

THE PEROXIDE CONTENTS OF ALLYL BROMIDE, ALLYL ALCOHOL AND LIGROIN

These tests were carried out in the usual way by shaking the sample with 10% ammonium thiocyanate solution and crystals of ferrous ammonium sulfate. The results are expressed in the following manner. The instant intense coloration obtained with the old samples of allyl bromide and alcohol is assigned the value 4. The exceedingly faint color of the blank is considered to be 0. Intermediate values represent intermediate color intensities.

Material tested	No.	Treatment of material	Peroxide test
Freshly prepared allyl bromide	1	None	0
	2	Oxygen passed through sample for five minutes in diffused light	1
Allyl bromide prepared two months previously	3	None	4
	4	Stood with diphenylamine a few hours at room temperature	4
	5	Distilled	2
	6	Distilled from diphenylamine	2
	7	4.0 g. allyl bromide, 1.0 g. hydrogen bromide, and 0.1 g. diphenylamine stood in dark in bomb tube for nineteen hours, decanted material	0
	8	Same, distilled material	0
Eastman allyl alcohol, received a few months previously	9	None	4
	10	Distilled	1
	11	Stood with diphenylamine a few hours at room temperature	4
Ligroin, washed with concd. sulfuric acid a few months previously, and distilled, b. p. 32-35°	12	None	1

Many materials were tried as antioxidants. Naturally the common ones such as diphenylamine, phenyl- β -naphthylamine, hydroquinone, mercaptobenzothiazole, thiophenol and thiocresol were tried and found to be effective,⁶ as well as some weaker ones such as resorcinol and dimethylaniline. On the other hand, potassium cyanide, ammonium bromide, and diphenyl ether were without effect on the addition in the presence of oxygen. This indicates that the mere presence of an ammonia nitrogen atom is not the important factor, but the presence rather of a system

(6) The addition proceeds with approximately the same velocity in the presence of most antioxidants although the velocity is slightly higher (with and without solvents) with diphenylamine than with hydroquinone. The presence of a little tertiary butyl isocyanide, however, increases the velocity of the normal addition three- or four-fold.

which under the conditions of the experiment may selectively take away the oxygen from peroxides.

It must be borne in mind, however, that since the antioxidants mentioned above as well as glacial acetic acid and ferric and aluminum chlorides all lead to the same final result, namely, the formation of 1,2-dibromopropane even in the presence of peroxides, it is highly probable that the mechanism of their effect may differ widely from case to case.

During an experience covering about 500 additions, we have (with certain minor exceptions which will be duly noted in their places) never observed any difference between the behavior of a reaction mixture freed beforehand from peroxides and run *in vacuo*, and that of one run *in vacuo* or in air in the presence of a good antioxidant. In describing the effect of temperature, solvent, light, etc., on the addition reaction, we shall therefore refer to runs made under "peroxide-free" conditions without specifying necessarily in each case by which of the two methods just mentioned those conditions were attained.

For the proper appreciation of the entire subject matter, the reader should note that the following factors were evaluated and shown to be without effect: the addition products, 1,2- and 1,3-dibromopropanes (Table VI); phosphorus pentoxide and phosphoric acid (Table VI); traces of water when the reaction mixture was not dried (Tables I and II); drying agents, the time of drying, and the concentration of hydrogen bromide (Table I); and surface catalysts (Table XVII, to be discussed later).

TABLE VI

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF THE ADDITION PRODUCTS, PHOSPHORUS PENTOXIDE AND PHOSPHORIC ACID

No.	Material added	Moles	Air ^a	Yield, %	Reaction, time	% 1,3 ^b	Remarks
73	1,2-Dibromopropane	0.12	Present	94	3 days	86	
74	1,3-Dibromopropane	.12	Present	87	3 days	86	
235	1,2-Dibromopropane	1.0	Absent	94	12 days	36	} { 2.5 moles HBr used
248	1,3-Dibromopropane	1.0	Absent	99	12 days	21	
168	Phosphoric acid	0.01	Present	100	46 hours	91	
175	Phosphorus pentoxide	.1	Present	96	16 hours	90	
174	Phosphorus pentoxide	.1	Present	96	5 minutes	92	Run 20 cm. from 500-watt lamp
192	Phosphorus pentoxide	.05	Absent	46	42 hours	<30	
199	Phosphorus pentoxide	.17	Absent	27	16 hours	<30	
220	Phosphoric acid	.12	Absent	30	20 hours	10	

^a Except where noted otherwise, 1.5 moles of hydrogen bromide was used. When air was present, the bomb tubes were sealed off without evacuation, and without drying or distillation of the reaction mixture. Nos. 174 and 175 were shaken for an hour at -75° before they were allowed to warm to room temperature. When air was absent, the reaction mixtures were dried and distilled *in vacuo* into another bomb tube. This latter tube contained phosphoric acid or phosphorus pentoxide when these substances were present. ^b See corresponding note to Table I.

2. The Temperature Effect.⁷—Our experiments on the effect of changes of temperature on the addition of hydrogen bromide to allyl bromide were conducted at temperatures ranging from -75 to 100° . Some of these results are given in Table VII and they are summarized graphically in Fig. 1. Within the limits investigated by us the effect of increase of temperature is to increase the velocity of both the normal 1,2 addition and the peroxide-catalyzed 1,3 addition. The latter addition, however, has a temperature coefficient 1.5–2 times that of the former.

TABLE VII

THE EFFECT OF TEMPERATURE ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE ABSENCE OF SOLVENTS

No.	Temp., °C.	Yield, %	Reaction time	% 1,3- ^b	Remarks
Air present. 1.5 moles of hydrogen bromide used. Reaction mixture sealed off with air at -75° without drying					
427	-75	73	1 hour	95	Old allyl bromide reacted during solution of hydrogen bromide
66	0	62	10 days	16	
67	0	65	10 days	25	
123	0	72	21 days	46	
112	0	100	48 hours	92	
396	0	100	6 days	80	Reaction mixture dried and distilled. Dried air admitted
121	7	64	11 days	18	
101	9	90	15 days	71	
122	14	100	10 days	95	
102	16	87	9 days	65	
124	20	100	6 days	90	
125	28	100	3 days	93	
127	37	100	3 days	84	
Air absent. 1.5 moles of hydrogen bromide used. Reaction mixture dried and distilled, run <i>in vacuo</i>					
132	0	81	50 days	13	Mean of two results
133	14	72	18 days	8	
131	29	71	6 days	17	Mean of two results
134	37	92	6 days	43	Mean of three results
190	56	99	23 hours	90	Mean of three results
289	56	78	13 hours	63	
309	56	75	20 hours	50	
314	56	91	28 hours	68	
146	76	99	12 hours	88	Mean of three results
319	76	99	18 hours	82	Dried overnight with a very large quantity of
158	100	100	24 hours	89	Mean of two results P_2O_5
376	76	75	13 hours	26	0.011 mole hydroquinone present
383	76	86	13 hours	16	.011 mole resorcinol present
416	76	99	16 hours	16	.014 mole diphenylamine present. Mean of two
390	100	89	13 hours	33	.011 mole hydroquinone present results
434	100	100	16 hours	18	.014 mole diphenylamine present

^b See corresponding note to Table I.

(7) All of the experiments of which the results are reported in this section were made in the dark in the absence of solvents.

So marked is the difference that at low temperatures, large amounts of 1,2-dibromopropane are formed even in the presence of air, if the initial peroxide content of the allyl bromide is low. Otherwise, the 1,3-dibromide is formed (Note No. 427). On the other hand, at high temperatures the formation of 1,3-dibromopropane is so rapid that the merest traces of peroxide, even when air is carefully removed, are sufficient to cause the formation of this product.

This explanation accounts for certain small discrepancies between the results obtained at high temperatures. At such temperatures, where the 1,3 addition catalyzed by peroxides is greatly accelerated, even the slightest traces of peroxides affect the course of the reaction and cause the formation of a greater amount of the 1,3-dibromide than would have been formed had the reaction been carried out at a lower temperature.

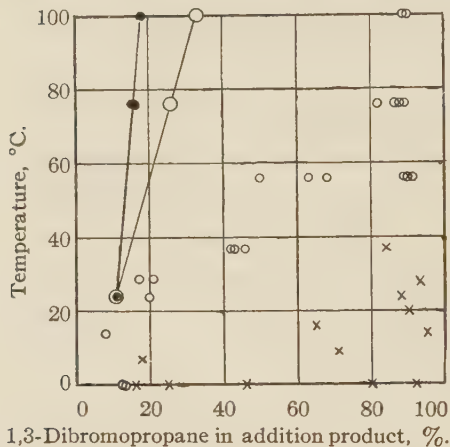


Fig. 1.—The effect of temperature on the addition of hydrogen bromide to allyl bromide, a summary of Table VII except that results for 24° are condensed from Tables I and II. X represents results obtained in the presence of air; small open circles, in the absence of air; large open circles, in the absence of air and the presence of hydroquinone; and small solid circles, in the absence of air and the presence of diphenylamine.

For this reason, if at a high temperature peroxides are present and an antioxidant is to be used, the latter must be extremely effective if all peroxide effect is to be eliminated. We have noted considerable variation in this respect among the antioxidants which we have employed. However, if the antioxidant used is one of the best the amount of 1,3-dibromopropane formed is, within the limits of error, the same as that obtained at low temperatures. *In vacuo* and under so-called "peroxide-free conditions," but in the absence of an antioxidant, we have not obtained such clear-cut results. It is extremely difficult under the conditions of the experiment without an effective antioxidant to eliminate all traces of peroxides, and so reactions run under the conditions just described uniformly yield more 1,3-dibromopropane with increasing temperature.

It is easy to see that under these circumstances workers whose attention has not been called to the effect of the peroxide in directing the addition might interpret the increase in yield of 1,3-dibromopropane with increasing temperature as a primary temperature effect. *In fact, it has been stated that high temperature favors the formation of the 1,3-, and low tempera-*

ture the 1,2-dibromide. This statement is true (as our own data testify) but not exactly in the sense intended. That the temperature effect is subsidiary to the peroxide effect is clearly shown by the runs made in the presence of antioxidants where a large increase in temperature causes scarcely any change in the composition of the addition product. In the absence of such antioxidants, heat favors the formation of 1,3-dibromopropane because peroxides are more effective in causing formation of this product at high temperatures than they are at low temperatures.

3. The Solvent Effect.—In view of what has already been said about the effect of peroxides on the addition of hydrogen bromide to allyl bromide, it was necessary to take this factor into account in the study of the effect of solvents.

The first important fact to be noted from our work with various solvents is that in the dark under "peroxide-free conditions" (presence of antioxidants) all the solvents used were without effect on the direction of addition, *i. e.*, the product was always about 90% 1,2-dibromopropane: (water, Table IX; acids, Table X; aqueous acetic acid, Table XI; ligroin, chloroform, carbon tetrachloride, carbon disulfide, Table XII; acid halides, Table XIII). In particular, the dielectric constant of the solvent made no detectable difference in the composition of the addition product under peroxide-free conditions, although this constant varied from 1.83 in the case of ligroin (pentane) to 80.0 in the case of water (Table VIII). That the dielectric constant may have an effect upon the velocity of addition is self-

TABLE VIII

THE CORRELATION BETWEEN THE DIELECTRIC CONSTANT OF THE SOLVENT AND THE DIRECTION OF ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

The results listed in this table represent what we believe to be the best values from Tables VI, IX, X, XII and XIII. The dielectric constants of the pure solvents are for a temperature of 20°.

Solvent	Dielectric constant	% 1,3 (remainder of product is 1,2)		
		Air present	Air absent Antioxidant Absent	Air absent Antioxidant Present
Pentane (ligroin)	1.83		90	11
Carbon tetrachloride	2.24		54	12
Carbon disulfide	2.6	95	14	
Propionic acid	3.19		13	
1,2-Dibromopropane	4.35	86	36	
Chloroform	5.05	87	42	12
Acetic acid	6.4	16	12	
Acetyl bromide	16.5	25	15	
Benzoyl bromide	19.0	20		
Formic acid	47.9		11	
Water	80.0	85	16	11
1,3-Dibromopropane		86	21	
β -Phenylpropionic acid		11		
Hydrogen bromide	3.82			
Allyl bromide	7.0	89	15	11

TABLE IX

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF WATER

No.	Moles HBr	Moles H ₂ O	% ^c HBr	Air ^d	Yield, %	Reaction time	% 1,3- ^e	Remarks
Runs in which less than 1% of water was present								
Run at 0°								
114	1.51	0.03 ^a		Present	91	48 hours	95	
395	1.51	.13		Present	100	4 days	84	
430	1.50	.05		Present	97	22 days	29	
Run at room temperature								
126	1.50	.03 ^a		Present	100	3 days	96	(28°)
337	1.53	.02 ^b		Present	97	17 hours	87	
330	1.53	.02 ^b		Absent (1)	32	21 hours	18	
336	1.50	.02 ^b		Absent (1)	100	10 days	63	
351	1.56	.03 ^a		Absent (1)	81	7 days	21	
218	1.53	.054		Absent (2)	100	19 hours	84	
399	1.50	.055		Absent (1)	98	7 days	8	0.014 mole diphenylamine present
Run at 76°								
343	1.50	.03 ^a		Absent (1)	98	9 hours	90	
418	1.50	.054		Absent (1)	99	16 hours	18	0.014 mole diphenylamine present
Runs in which more than 5% of water was present								
Run at room temperature								
358	2.54	1.98	85.2	Present	100	40 hours	83	Mean of two results
357	2.52	1.98	85.2	Absent (1)	100	41 hours	83	Mean of three results
327	2.26	1.51	87.1	Absent (2)	99	4 days	16	
400	2.52	1.97	85.0	Absent (1)	89	4 days	11	0.014 mole diphenylamine present
Run at 76°								
342	2.55	1.90	85.8	Absent (1)	81	9 hours	61	
384	2.55	2.01	85.0	Absent (2)	100	13 hours	76	
417	2.55	2.00	85.0	Absent (1)	100	16 hours	21	0.014 mole diphenylamine present
Run at 100°								
298	1.98	2.02	81.5	Absent (2)	100	16 hours	87	
Runs in which about 50% of water was present								
Run at room temperature								
F3	2.78	18.8	40.0	Present	<2	108 days	..	
F4	5.00	33.6	40.0	Present	<5	40 days	..	Run 60 cm. from 100-watt lamp
Run at about 125°								
290	3.93	26.4	40.0	Present	<10	11 hours	..	Only tar obtained

^a Estimated. Allyl bromide saturated with water at room temperature before addition of hydrogen bromide. ^b Same as ^a but saturated at 0°. ^c Ratio of weight of hydrogen bromide to weight of hydrogen bromide plus water. ^d When air was present, the bomb tubes were sealed off with air at -75°. When air was absent, it was removed (1) by evacuation of the bomb tube without distillation or (2) by evacuation and subsequent vacuum distillation. ^e See note ^b to Table I.

TABLE X

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN GLACIAL ACETIC ACID
(INCLUDING ALSO A FEW RUNS IN OTHER ACIDS)

No.	Moles HBr	Moles acid	Air ^a	Yield, %	Reaction time	% 1,3- ^b	Remarks
Run in the dark at room temperature							
Acetic acid							
F1	1.87	8.88	Present	<5	22 hours	..	
X1	3.73	15.8	Present	>60	7 days	5	
X3	2.80	6.59	Present	89	15 days	8	
X6	2.64	4.55	Present	96	13 days	5	
280	2.51	1.50	Present	100	4 days	19	
406	2.50	1.50	See remark	100	45 hours	16	Bomb tube filled with oxygen
352	2.50	1.50	Absent	99	42 hours	12	
Other acids							
34	1.50	1.50	Present	92	7 days	11	β -Phenylpropionic acid
297	2.66	1.50	Absent	100	7 days	13	Propionic acid
325	2.49	1.50	Absent	96	43 hours	10	Formic acid ^c
414	2.43	1.50	Absent	76	15 hours	12	Formic acid, mixture flushed with N ₂ before solution of HBr
Acetic acid							
Run at 76°							
197	1.50	1.49	Present	99	17 hours	17	
Run near 100-watt ^d lamp at room temperature							
X2	4.0	8.0	Present	85	66 hours	10	15 cm. from lamp, mean of three results
X11	1.50	0.33	Present	100	5 days	40	15 cm. from lamp
Run near 500-watt ^d lamp at room temperature							
179	1.51	1.50	Present	9	30 min.	Mostly 1,2-	15 cm. from lamp
186	2.3	1.50	Present	98	15 hours	26	20 cm. from lamp
345	2.58	1.50	Absent	100	14 hours	24	15 cm. from lamp
413	2.66	1.50	Absent	99	15 hours	17	15 cm. from lamp, 0.011 mole quinone present, mixture flushed with nitrogen before solution of hydrogen bromide
Run near 500-watt ^d lamp at temperature of 4-7°							
266	2.66	1.50	Present	95	16 hours	42	20 cm. from lamp, mean of two results
349	2.50	1.50	Absent	76	8 hours	49	12 cm. from lamp
436	2.50	1.50	See remark	98	15 hours	75	7.5 cm. from lamp, allyl bromide and acetic acid flushed with, and bomb tube filled with, oxygen
437	2.50	1.50	Absent	92	15 hours	70	7.5 cm. from lamp, 0.014 mole of diphenylamine present, allyl bromide and acetic acid flushed separately with N ₂

^a When air was present, the bomb tubes were sealed off with air at -75°, without drying of the reaction mixture. Except for No. 437, air was removed from the runs with

acetic acid by simply evacuating the bomb tubes. In the runs with other acids, and No. 437 with acetic acid, the hydrogen bromide and allyl bromide were dried and distilled *in vacuo* into the solvent.

^b See corresponding note to Table I.

^c Under the experimental conditions, formic acid was largely decomposed into water and carbon monoxide. Special precautions were taken in handling and opening the bomb tubes because of the large pressures developed.

^d The 100-watt lamp was an ordinary frosted one. The 500-watt lamp was an incandescent projection lamp.

TABLE XI

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN AQUEOUS ACETIC ACID SOLUTION

No.	Moles HBr	Moles acetic acid	Wt. AcOH	Air ^a	Yield, %	Reaction, time	% 1,3- ^b	Remarks
			wt. (AcOH + H ₂ O) %					
Run in the dark at room temperature								
276	2.52	1.50	97.7	Present	100	4 days	28	
237	1.53	1.50	97.0	Present	93	73 hours	46	
236	1.81	1.50	93.9	Present	98	73 hours	71	
356	2.50	1.50	90.0	Present	100	40 hours	64	
140	1.54	1.53	90.0	Present	96	9 days	82	
408	2.54	1.20	75.0	Present	100	42 hours	82	
409	2.52	1.20	75.0	Present	90	45 hours	18	0.011 mole hydro- quinone present
338	2.55	1.51	90.3	Absent	100	5 days	24	} Allyl bromide and acetic acid flushed with N ₂ before solution of HBr
355	2.54	1.50	90.0	Absent	95	41 hours	15	
360	2.50	1.50	79.0	Absent	92	43 hours	26	
410	2.61	1.20	75.0	Absent	100	42 hours	33	
Run near 500-watt lamp ^d at room temperature								
255	1.68	1.50	97.8	Present	97	16 hours	50	13 cm. from lamp
275	2.50	1.50	97.8	Present	100	16 hours	38	15 cm. from lamp
348	2.55	1.50	90.2	Absent	100	14 hours	63	15 cm. from lamp

^a When air was present, the bomb tubes were sealed off with air at -75° without special treatment of the reaction mixture. Otherwise, the bomb tubes were simply evacuated. ^{b,d} See corresponding notes to Tables I and X, respectively.

evident. However, in addition to this notion, many chemists consider also the position taken by the addenda to be influenced by the solvent.⁸ The reference to the list of authors is not at all indicative of the extent to which this notion is prevalent. There are many more scattered allusions to that effect in the literature and the notion had been widely accepted by the chemists with whom the authors discussed this problem prior to the completion of their work.

Indeed, Table VIII shows that if no attention is paid to the peroxide content of the allyl bromide and the "antioxidant" effect of the solvent used, it is easy to obtain results of a highly deceptive nature. For instance, a series of additions made in the presence of air, with solvents of high di-

(8) Michael and Zeidler, *Ann.*, **385**, 265 (1911); Ipatiev and Ogonowski, *Ber.*, **36**, 1988 (1903).

TABLE XII

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF LOW-BOILING PARAFFIN HYDROCARBONS, CHLOROFORM, CARBON TETRACHLORIDE, AND CARBON DISULFIDE

Except as noted otherwise, the runs listed in this table were dried, distilled *in vacuo*, and sealed off without the entrance of air, as described in the experimental part, and the additions took place in the dark at room temperature. 1.5 moles of solvent were used.

No.	Moles HBr	Solvent	Yield, ^a %	Reaction time	% 1,3- ^b	Remarks
A1	1.50	Heptane	70	6 days	92	Run 20 cm. from 100-watt ^d lamp. Sealed off with air without drying or distillation
257	2.55	Chloroform	72	9 days	92	Undried air admitted
72	1.54	Carbon disulfide	84	6 days	95	Sealed off with air without drying or distillation
147	2.25	Ligroin (1) ^c	68	13 days	90	Mean of three results
316	2.25	Ligroin (2)	75	15 days	90	
202	2.45	Ligroin (1)	79	35 days	92	Mean of two results. Run at 0°
247	1.79	Ligroin (1)	39	25 days	90	Run at 0°
329	2.50	Ligroin (3)	87	48 hours	7	0.02 mole anh. FeCl ₃ added (cf. Table XVI)
269	2.67	Chloroform	90	9 days	88	Mean of two results
306	2.52	Chloroform	73	14 days	42	
318	2.52	Chloroform	89	16 days	89	Dried overnight with large excess of P ₂ O ₅
304	2.55	Chloroform	57	28 days	33	Run at 0°
183	2.04	Carbon tetrachloride	72	13 days	83	
293	2.64	Carbon tetrachloride	66	9 days	67	
305	2.56	Carbon tetrachloride	48	10 days	54	
315	2.56	Carbon tetrachloride	77	15 days	77	Dried overnight with large excess of P ₂ O ₅
307	2.50	Carbon tetrachloride	28	31 days	7	Run at 0°
148	2.60	Carbon disulfide	53	13 days	14	Mean of two results
187	2.50	Carbon disulfide	91	14 hours	95	Mean of three results. Run 15 cm. from 500-watt ^d lamp
371	2.55	Ligroin (3)	18	13 days	20	0.011 mole hydroquinone
397	2.50	Ligroin (3)	38	26 days	11	0.011 mole hydroquinone
401	2.50	Carbon tetrachloride	59	26 days	12	0.011 mole hydroquinone
402	2.50	Chloroform	78	26 days	12	0.011 mole hydroquinone
403	2.50	Ligroin (3)	57	26 days	11	0.014 mole diphenylamine
404	2.55	Carbon tetrachloride	74	26 days	12	0.014 mole diphenylamine
405	2.50	Chloroform	81	26 days	12	0.014 mole diphenylamine

^a The yields in this table represent the weight of dibromopropanes recovered after removal of the solvent and allyl bromide by fractional distillation. Because of comparatively large losses in working with very small quantities of material 10% or more should be added to these values to make them comparable with the yields as given in other tables.

^{b,d} See corresponding notes in Tables I and X, respectively.

^c Commercial petroleum ether was washed several times with concentrated sulfuric acid and then with water, dried, and fractionally distilled. From various lots, different fractions were collected which are noted in the table by numerals: (1) 30–41°, (2) 41–60° and (3) 32–35°. For purposes of calculation, the ligroin is assumed to be pentane.

electric constant and some ability to act as antioxidants on the one hand, and with solvents of low dielectric constant and no ability to act as antioxidants on the other, might easily suggest that high dielectric constants favored the formation of the 1,2-, and low the formation of the 1,3-dibromide. However, as soon as we introduce the use of antioxidants as an extreme precaution, the apparently consistent series has no foundation. Thus, of about a dozen different solvents of widely varying properties that were tried, none affected perceptibly the order of addition when the effect of oxygen was removed, although the rate of addition with these solvents may have varied by a factor of one hundred or more. We are thus forced to the conclusion that the dielectric constant of the solvent has no direct effect on the direction of addition but that the solvent may affect the stability of peroxides, resist the effect of oxygen, or affect the relative velocities of the two competing reactions. The resistance of some solvents to the oxygen effect may be due to any or all of three causes: first, the stability of the peroxides of allyl bromide may vary with the solvent (note particularly the striking diminution of the antioxidant effect of acetic acid upon dilution with water, Table XI, and how it may be restored by the addition of an antioxidant); second, the peroxide content of the solvent itself may vary (Table V, note also the effect of small quantities of benzoyl peroxide, Table III); and third, the variation due to the wide differences in the velocities of addition to give 1,2-dibromopropane, *i. e.*, the velocity of the normal addition may be more affected by the solvent than that of the peroxide-catalyzed addition.

It is interesting to note here that apparently the dielectric constant of the solvent has considerable influence on the velocity of addition, yet there is no simple direct relationship. One might say from a superficial examination of the accumulated facts that the higher the dielectric constant of the solvent, the greater will be the velocity of addition. Nevertheless, careful examination shows that while the statement is confirmed by the runs with antioxidants with ligroin, carbon tetrachloride, and chloroform in Table XII (the yield in twenty-eight days follows exactly the order of increasing dielectric constant), and is also true in comparing formic and acetic acids, it does not hold when different types of solvents are compared. Thus, both allyl bromide and acetyl bromide have higher dielectric constants than acetic acid, but the addition in the latter solvent is far faster than in the absence of a solvent or in the presence of acetyl bromide. Another set of results which are difficult to explain solely on the basis of dielectric constants are those with water (Table IX). Considering only the runs in which the principal product was 1,2-dibromopropane, it may be seen that the addition of a little water (85% aqueous hydrogen bromide) accelerates the addition, but in 40% aqueous hydrogen bromide, practically no addition takes place.

TABLE XIII

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF ACETYL BROMIDE AND BENZOYL CHLORIDE

1.5 moles of acetyl bromide was used as solvent in all of these runs excepting two, where note is made of the use of benzoyl chloride.

No.	Moles HBr	Air ^a	Yield, %	Reaction time	% 1,3- ^b	Remarks
Run in the dark at room temperature						
141	1.70	Present	91	11 days	25	
378	2.50	Present	99	12 days	46	
260	2.33	Present	^c	9 days	20	Benzoyl chloride
411	2.50	Absent	96	14 days	15	
Run at 76°						
256	1.63	Present	92	16 hours	74	
354	2.54	Present	97	8 hours	55	
344	2.58	Absent	93	9 hours	31	
353	2.57	Absent	94	9 hours	24	
Run near 500-watt lamp ^d at room temperature						
180	1.51	Present	17	30 min.	..	Run 15 cm. from lamp
188	2.14	Present	100	15 hours	89	Run 20 cm. from lamp
265	2.66	Present	100	19 hours	92	Run 15 cm. from lamp
347	2.56	Absent	100	14 hours	91	
261	2.45	Present	^c	12 hours	92	Run 15 cm. from lamp, benzoyl chloride

^a When air was present, the bomb tubes were sealed off with air at -75° without special treatment of the reaction mixture. When air was absent, it was generally removed by evacuation of the bomb tube without drying or distillation of the reaction mixture. In No. 411, nitrogen was passed through the mixture of allyl bromide and acetyl bromide before the solution of hydrogen bromide. The whole reaction mixture was then dried and distilled *in vacuo*.

^{b,d} See corresponding notes to Tables I and X, respectively.

^c Attempts were made to remove benzoyl chloride from the reaction products by washing with sodium carbonate, sodium hydroxide and concentrated sulfuric acid, but without much success. Because of the large losses of material, nothing can be stated about the yields except that they were probably good.

It is possible that the solvent may affect the association of allyl bromide, if allyl bromide can be associated. Mixtures of allyl bromide and a solvent were made up to find the relation between the mole fraction of the solvent in the mixtures and their indices of refraction. In Fig. 2 the results of these experiments with heptane, acetic acid, chloroform, 1,3-dibromopropane and carbon disulfide are plotted. With none of these substances was the index of refraction exactly a linear function of the mole fraction of allyl bromide in the mixtures. The curves for mixtures of allyl bromide and heptane or carbon disulfide lie well below the straight lines joining the indices of refraction of allyl bromide and the solvents used, but the curves for mixtures of allyl bromide with acetic acid, chloroform and 1,3-dibromopropane lie slightly above the corresponding straight lines. The deviation of the latter group of curves is small but well beyond the ex-

perimental error and may be explained by a slight contraction of volume on mixing the two liquids. The deviation of the curves for the mixtures with heptane or carbon disulfide is much larger and in the opposite direction. To explain this latter deviation by a change of volume on mixing the two liquids, we should have to assume that the mixture is of much greater volume than the sum of the individual volumes of the liquids of which the mixture is comprised. The deviation is so large that there may be some very unusual condition existing in these mixtures, such as association or compound formation.

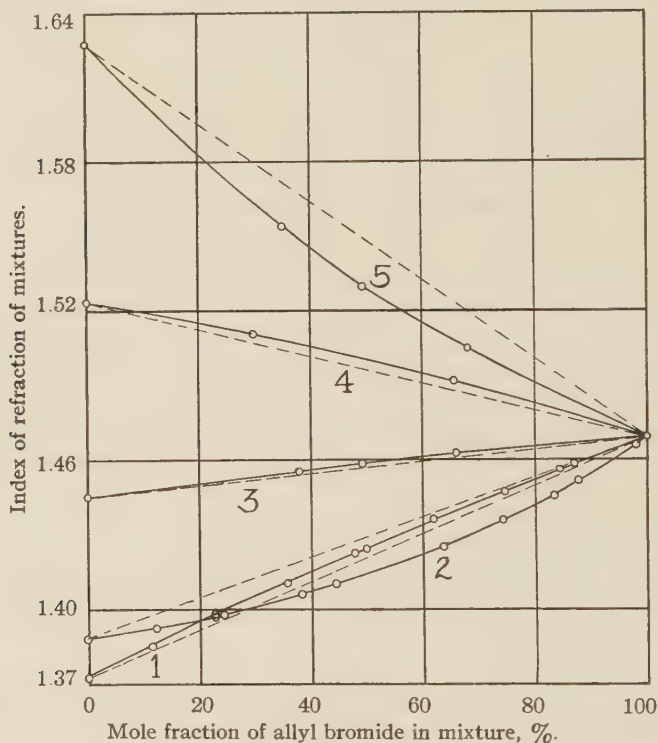


Fig. 2.—Indices of refraction of mixtures of allyl bromide with various solvents: (1) acetic acid, (2) heptane, (3) chloroform, (4) 1,3-dibromopropane, and (5) carbon disulfide. The straight broken lines are inserted to show the deviation of the curves from straight lines.

4. The Temperature Effect in Solvents.—Without undertaking a detailed analysis of the combined effects of solvent and temperature, it may be stated briefly that these effects are essentially independent of one another. All of the statements made about the temperature effects without a solvent and about the effect of solvents on the peroxide effect may be applied without change to reactions involving both solvents and change of

temperature. We have observed no instance where the presence of a solvent seriously affected the ratio of the temperature coefficients of the two addition reactions.

The resistance of glacial acetic acid to the peroxide effect at 76° , even in the presence of air (Table X), is rather remarkable. This property of resisting the effect of peroxides seems to be common to carboxylic acids, and to a lesser extent to the acid halides (Table XIII).

5. The Light Effect.—The effect of light on the addition of hydrogen bromide to allyl bromide was first studied with samples of the latter which *in vacuo* and in the dark reacted in ten days to give 80–90% of a product containing about 80% 1,2-dibromopropane. Under strong illumination, the addition was sometimes complete within thirty minutes (Table XIV), and the product was about 90% 1,3-dibromopropane. Temperature lowering to 5° had no effect upon the latter reaction except to slow it down.

TABLE XIV

THE EFFECT OF LIGHT ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

Except as noted otherwise, these reaction mixtures were dried and distilled as described in the experimental part. The additions took place in the absence of air at about 30° and at a distance of a few centimeters from a 500-watt incandescent projection lamp. 1.5 moles of hydrogen bromide was used.

No.	Distance from lamp, cm.	Yield, %	Reaction time	% 1,3. ^b	Remarks
173	18	100	20 min.	90	Sealed off with air without drying or distillation Mean of two results
X5	18	89	15 days	90	100-watt lamp used. Allyl bromide saturated repeatedly with HBr at -10°
150	15	100	45 hours	93	Mean of four results
162	20	100	42 hours	95	Dried overnight with large excess P_2O_5
176	15	99	30 min.	92	
206	15	99	60 min.	92	Thermometer ^a in bomb tube.
322	16	77	60 min.	92	Thermometer ^a in bomb tube. Mean of two results
341	13	100	60 min.	95	Thermometer ^a in bomb tube. Allyl bromide saturated with water. Reaction mixture not dried or distilled. Bomb tube evacuated
169	20	100	60 min.	93	Dried with Na_2SO_4 instead of P_2O_5 . Mean of three results
375	12	68	13 hours	82	0.011 mole hydroquinone present
391	12	94	14 hours	79	0.014 mole diphenylamine present
444	10	91	16 hours	65	0.029 mole thiocresol present
271	20	80	3 hours	92	Run at $5-10^{\circ}$, mean of two results
446	6.5	54	20 hours	39	Run at $5-6^{\circ}$, 0.048 mole thiocresol present

^a The thermometer in No. 206 showed that a maximum temperature of 54° was reached at the end of 18 min. and that the temperature dropped slowly thereafter to reach 33° at the end of the hour. The other three runs attained maxima of about 40° in about twenty minutes. All were at a temperature of -75° when started. No. 206 showed a definite decrease in the rate of temperature rise at about 30° . However, twelve minutes after starting, the temperature began to rise suddenly and rapidly from 31° . ^b See corresponding note to Table I.

The effect of antioxidants on the addition with full illumination will be discussed later.

Table XV shows that light of all wave lengths accelerates both reactions. In the absence of air and antioxidants, the short wave lengths have a

TABLE XV

THE EFFECT OF LIGHT FROM DIFFERENT SPECTRAL REGIONS UPON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

All of these reaction mixtures were dried, distilled, and run *in vacuo*.⁴ A 500-watt incandescent projection lamp was used for illumination. The glass color filters used were the products of the Corning Glass Works, and their names and characteristics are taken from the Corning catalog. When one limit of transmission of a filter is omitted, it is unknown and beyond the visible region. In those runs where the yields were too poor to isolate the addition product, the product was probably 1,3-dibromopropane. The additions took place at about 30–35°, and except as noted, 1.5 moles of hydrogen bromide was used.

No.	Color filter used	Trans- mission, Å.	Distance from lamp to bomb tube	Yield, %	Reaction, time	% 1,3- ^b	Remarks
224	Cardboard (blank)	None	12	0.2	30 min.	..	
225	Heat-resisting (H.R.) signal red	6200–	12	1	30 min.	..	
226	H.R. medium yellow	5500–	12	2	30 min.	..	
229	Dark theatre blue	3900–5200	12	11	30 min.	..	
230	Violet	–4800	12	1	30 min.	..	
227	Noviol O	3900–	12	25	30 min.	..	
231	Red-purple Ultra	3200–4200 { also >7200 {	12	47	30 min.	..	
221	Red-purple Ultra		14	97	55 min.	92	
240	Noviol O	3900–	12	78	50 min.	92	
239	Noviol C	4600–	12	65	50 min.	92	
438	H.R. signal red + Noviol C	6200–	8	100	3 hours	89	
213	39 mm. 2% aq. CuCl ₂ soln.	3400–7000	15	88	30 min.	92	
217	18 mm. sat. aq. K ₂ - Cr ₂ O ₇	5150– ⁹	15	100	4 hours	92	
0.014 mole of diphenylamine was also present in the following runs:							
419	Red-purple Ultra	3200–4200 also >7200	10	99	24 hours	70	1.75 moles HBr
420	Noviol C	4600–	10	98	24 hours	33	1.75 moles HBr
421	Noviol C + H.R. signal red	6200–	10	92	24 hours	18	1.92 moles HBr
424	Red-purple Ultra + 18 mm. 2.8% CuSO ₄ soln. ¹⁰	3200–4200	12	92	24 hours	59	1.92 moles HBr
432	Red-purple Ultra + 18 mm. 2.8% CuSO ₄ soln.	3200–4200	10	94	24 hours	74	1.98 moles HBr
425	18 mm. 2.8% CuSO ₄ soln. + Noviol C	4600–7000	12	95	24 hours	29	2.74 moles HBr
433	18 mm. 2.8% CuSO ₄ soln. + Noviol C	4600–7000	10	95	24 hours	61	2.01 moles HBr

^b See corresponding note to Table I.

(9) Bhagwat and Dhar, *J. Indian Chem. Soc.*, **7**, 913 (1930).

(10) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 273.

greater accelerating effect than the longer ones. All wave lengths accelerate the addition to form 1,3-dibromopropane much more than the normal addition and this dibromide is therefore formed to the extent of about 90%. The runs with diphenylamine show that the effect of infra-red radiation, like that of temperature, is only to exaggerate greatly the effect of small but significant quantities of peroxides. In the presence of this antioxidant, the peroxide-catalyzed reaction is inhibited and is replaced by the slower normal addition.

Light from the visible and near ultraviolet regions favors the formation of the 1,3-dibromide so strongly that even in the presence of large amounts of good antioxidants this product is formed to the extent of 30-75% depending upon the wave length and intensity of the radiation employed. Although it seems quite certain that the effect of the longer wave lengths is only to increase the effect of peroxides, the interpretation of the effect of the shorter wave lengths is less certain and will be discussed in connection with the effect of illumination on the addition in glacial acetic acid solution.

It has been shown that the addition of hydrogen bromide to allyl bromide is reversed by light in the presence of acid halides (Table XIII), heptane and carbon disulfide (Table XII) to give about 90% of 1,3-dibromopropane just as in the absence of a solvent. The effect in acetic acid solution is more complicated and to it we shall now confine our attention.

In the addition of hydrogen bromide to allyl bromide, acetic acid behaves as a moderately strong antioxidant. It is strong enough so that when it is used as a solvent, runs made at room temperature under strong illumination yield over 70% 1,2-dibromopropane, whether air is present or not. It is, however, noteworthy that glacial acetic acid becomes less effective in repressing the formation of 1,3-dibromopropane at 5° (Table X) where reactions run under the same illumination yield from 40-75% of the 1,3 dibromide (depending on the intensity of the illumination), a result quite at variance with the usual effect of decreased temperature, which is to favor the normal addition to give 1,2-dibromopropane.

These unusual results may be accounted for in either of two ways, dependent upon whether we assume that glacial acetic acid is as efficient an antioxidant at 5° in the light as it is at 30°.

(1) If we assume that the antioxidant properties of the acid are unimpaired at low temperatures, then we believe that there is no escape from the conclusion that visible and ultraviolet light slowly convert allyl bromide into a form which adds hydrogen bromide to give 1,3-dibromopropane even in the absence of peroxides. At room temperature, illumination could not greatly influence the composition of the addition products, since the rate of the normal addition is so high that reaction is complete before much conversion has occurred. At the lower tempera-

ture, however, where the rate of the normal reaction is low, the amount of conversion is greater and the proportion of the 1,3-dibromopropane formed is correspondingly increased.

(2) On the other hand, an explanation consistent with all the facts is that the antioxidant effect of the acetic acid decreases with the temperature (that it increases with the temperature is shown by No. 197 in Table X), and that light exaggerates the peroxide effect at all temperatures. That there is at least some peroxide effect in the light in glacial acetic acid at 5° is shown by the last two runs in Table X. The difference in yields is significant even if the difference in products is not. This viewpoint finds further corroboration in the addition of hydrogen bromide to allyl bromide in the absence of solvents and the presence of antioxidants in the light (Tables XIV and XV). The use of diphenylamine and hydroquinone at room temperature had a slight but decided effect with full illumination and a much larger effect with light of longer wave lengths in increasing the yield of 1,2-dibromopropane formed. A more powerful antioxidant, thiocresol, increased the yield of this product to 35% with full illumination. Under the combined effects of lowering the temperature of reaction to 5° and the use of this antioxidant, the yield of 1,2-dibromopropane was increased to 61%. This last result is in agreement with our other observations that the effectiveness of peroxides decreases with lowering of temperature. These results from Tables XIV and XV point to the conclusion that the yield of 1,3-dibromopropane could be still further decreased by the use of still better antioxidants.

The results discussed in the preceding paragraph strongly suggest that all the factors (including now the light effect) which influence the addition of hydrogen bromide to allyl bromide exert their influence only through their effects on the minute but significant quantities of peroxides or oxygen present in the materials.

6. The Effect of Metallic Salts.—The results of Table XVI (see also No. 329 in Table XII) show that anhydrous ferric and aluminum halides have a tremendous accelerating effect upon the normal addition. The velocity of the reaction is undoubtedly proportional to the amount of these metal salts present (*cf.* Nos. 320 and 365). Although the additions were allowed to proceed for six to eighteen hours at room temperature, we know definitely that they were complete long before that time. No. 333 was found to have reacted completely after eighteen hours at -75°, but we surmise from the vigorous boiling of the acetone-solid carbon dioxide bath fifteen or twenty minutes after the tube was put into it that the reaction was probably over in thirty minutes.

Copper salts have no effect on the direction of addition of hydrogen bromide to allyl bromide, but they may have a slight antioxidant and accelerating effect.

TABLE XVI

THE EFFECT OF IRON AND SOME IRON, ALUMINUM AND COPPER SALTS ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

Except as noted otherwise, these addition mixtures contained 1.5 moles of hydrogen bromide, were dried and distilled onto the catalyst, and were run in the dark, at room temperature, and in the absence of air.

No.	Catalyst	Moles of catalyst	Yield, %	Reaction, time	% 1,3- ^b	Remarks
193	Iron wire	0.0011	50	42 hours	18	Iron did not dissolve
320	Anhydrous FeCl ₃	.007	100	6 hours	7	Mean of two results
333	Anhydrous FeCl ₃	.007	100	17 hours	5	Run at -75°
365	Anhydrous FeCl ₃	Trace ^a	29	18 hours	20	
331	Hydrated FeCl ₃	0.02	97	21 hours	8	Allyl bromide satd. with water at 0°. Bomb tube evacd. Re-actn. mixt. not dried or distd.
359	Hydrated FeCl ₃	.009	93	17 hours	8	Reaction mixture not dried or distd. 0.027 mole H ₂ O added.
332	Anhydrous AlBr ₃	.009	100	18 hours	5	
194	Cupric bromide	.00028	62	40 hours	18	
380	Cupric bromide	.01	83	11 days	16	
310	Cuprous bromide	.008	39	20 hours	10	
381	Cuprous bromide	.008	74	4 days	16	

^a A single minute crystal of ferric chloride (estimated to be about 0.000005 mole) was used. This small amount was sufficient, however, to impart a faint but distinct color to the reaction mixture. The other runs with the anhydrous salt were so darkly colored that they were opaque. ^b See corresponding note to Table I.

7. The Effect of Surface Catalysts.—The first two runs listed in Table XVII show that neither the glass surface nor materials within the glass affect the velocity of the reaction or the product formed. In the presence of silica gel and asbestos, however, the reaction is much faster

TABLE XVII

THE EFFECT OF SURFACE CATALYSTS UPON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

In all of these runs, 10 g. of allyl bromide containing 1.5 moles (10 g.) of hydrogen bromide was dried and distilled into the bomb tube containing the catalyst, and was sealed off without the entrance of air. The additions took place in the dark at room temperature.

No.	Catalyst	Weight of catalyst, g.	Yield, %	Reaction, time	% 1,3- ^b	Remarks
278	None		87	9 days	18	From Table I, for comparison
157	Broken Pyrex	20	85	9 days	20	
263	Glass wool	1.6	79	7 days	10	
264	Asbestos ^c	5.0	98	5 days	10	Mean of three results
311	Asbestos ^d	5.0	77	18 hours	8	
317	Asbestos ^e	4.3	71	67 hours	15	
312	Silica gel	5-10	98	18 hours	10	

^b See corresponding note to Table I.

^c Commercial acid-washed and ignited asbestos fiber.

^d Material from same source extracted with concentrated hydrochloric acid for several days, washed, and dried.

^e Same material used in run No. 311 washed, dried, and used over again.

but the composition of the product is unchanged. That this observed acceleration was due to iron salts was indicated by the deep red color of the reaction mixtures. Furthermore, when the asbestos was extracted with acid, the color produced was quite faint, and when this same asbestos was used over again a second time, there was no color in the presence of the reaction mixture and the yield was definitely less in four times the duration of the previous run, a fair indication that as iron salts were removed, the asbestos lost its activity. All of these runs point to the conclusion that the addition of hydrogen bromide to allyl bromide in the liquid phase is a homogeneous reaction.

General Conclusions

The results described in this paper have certain bearings on the various general theories of addition to the double bond which have from time to time been advanced. Any such theory which neglects the effect of the peroxide content of the unsaturated compound can derive no support from the behavior of allyl bromide. In particular, the reactions of this substance are definitely at variance with the idea that the dielectric constant of the solvent controls the direction of addition. Further work (which will be published shortly) on allyl chloride, vinyl bromide, butene-1, propylene, and other unsaturated substances fully confirms the results herein described and indicates that the peroxide content of the unsaturated compound is at least an important, and probably the dominant, factor controlling the velocity and direction of many addition reactions. In fact, so widespread does the peroxide effect appear to be that most of the data recorded in the literature probably need to be revalued before they can be used for or against any general theory of addition. One thing at least is certain: before applying the reactions of any particular compound in favor of any theory, the question of whether or not the reactions of this compound are seriously affected by its peroxide content must first be decided.

The unusual results obtained in the study of the addition of hydrogen bromide to allyl bromide show the need of extension of work of this type to other olefins and other unsymmetrical reagents¹¹ as well as to conjugated systems. Work along these lines has been actively under way in this Laboratory for some time, and we hope to publish shortly our other findings.

Experimental Part

1. Removal of Allyl Bromide from Mixtures of 1,2- and 1,3-Dibromopropanes.—

It was planned in this work to determine the composition of the addition products by their indices of refraction. This method made necessary the removal of allyl bromide

(11) The unusual addition of mercaptans and of sodium and potassium alkyls to styrene may thus be viewed from an entirely new viewpoint. The addition reactions of this substance are now under investigation in this Laboratory.

from the dibromopropanes. The common methods for effecting similar removals were shown to be unsatisfactory when working with small quantities of materials. Even fractional distillation followed by washing with concentrated sulfuric acid and another fractional distillation was found to be inadequate for removing allyl bromide from a synthetic mixture of the two dibromopropanes, as shown by the index of refraction of the mixture.

The method finally adopted had its inception in the well-known activity of the bromine in allyl bromide as compared with that in the dibromopropanes. Many amines react quite rapidly with allyl bromide, the tertiary amines to give water-soluble substituted ammonium salts, while under the same conditions, no appreciable reaction takes place with the dibromopropanes. Dimethylaniline was the reagent chosen for our work to accomplish the removal of allyl bromide from 1,2- and 1,3-dibromopropanes, and its use is justified by the experiments in Table XVIII. Detailed directions concerning our use of this reagent will be given presently.

TABLE XVIII

THE REMOVAL OF ALLYL BROMIDE FROM THE DIBROMOPROPANES WITH DIMETHYLANILINE

A. 10.0 g. of a mixture of 1,2- and 1,3-dibromopropanes having n_D^{20} 1.5217 was mixed with 2.5 g. of allyl bromide. Several such mixtures were treated with dimethylaniline according to the standard procedure for different lengths of time to determine how much time was required for complete removal of the allyl bromide:

Hours of treatment	11	16	24
n_D^{20} of product	1.5172	1.5217	1.5216

B. A mixture having a composition by weight of the dibromopropanes corresponding to an index of refraction of 1.5215 was mixed with varying amounts of allyl bromide so that the total weight of each ternary mixture was 12.5 g. The allyl bromide was then removed according to the standard procedure:

Weight % of allyl bromide in ternary mixt.	1	2	5	10
n_D^{20} of mixture after removal of allyl bromide	1.5216	1.5215	1.5214	1.5214

C. 10.0 g. each of mixtures of 1,2- and 1,3-dibromopropanes of different compositions were each mixed with 2.5 g. of allyl bromide which was then removed according to the standard procedure.

Mixture no.	1	2	3	4	5
Mole fraction 1,3-, %	5.3	28.9	55.2	76.2	94.7
Mole fraction 1,2-, %	94.7	71.1	44.8	23.8	5.3
n_D^{20} calculated ^a	1.5196	1.5204	1.5213	1.5221	1.5230
n_D^{20} obsd. before addn. of allyl bromide	1.5196	1.5205	1.5215	1.5223	1.5230
n_D^{20} after addn. of allyl bromide, calcd. ^a	1.5071	1.5078	1.5085	1.5091	1.5097
n_D^{20} after removal of allyl bromide, obsd.	1.5195	1.5205	1.5214	1.5222	1.5228

^a Calculated on the assumption that the index of refraction of the mixture is a linear function of its composition.

We obtained the following indices of refraction of the pure dibromopropanes (Eastman Kodak Co. products): n_D^{20} 1,2-, 1.5194; 1,3-, 1.5232. The indices of refraction of mixtures of these two compounds is shown by Table XVIII-C to be a linear function of composition. Using an Abbé refractometer, it was possible to ascertain the composition of mixtures of these addition products within $\pm 5\%$.

2. **Technique of Preparation of Reaction Mixture.**—Most of the work recorded in the literature, and the first two runs made by us, were made by repeated saturations of the allyl bromide with hydrogen bromide at about -10° . In the intervals between saturations, the mixtures were allowed to warm up to room temperature, or were heated.

This method is slow and time-consuming because of the low solubility of hydrogen bromide in allyl bromide at -10° .

To avoid these disadvantages, it was decided to dissolve sufficient hydrogen bromide in the allyl bromide in one step by cooling the allyl bromide to -75° . A simple apparatus (Fig. 3) was finally devised which enabled us also to exclude moisture and air, and which by a simple modification made it possible to introduce dry gases. The technique of carrying out an addition under these circumstances was as follows.

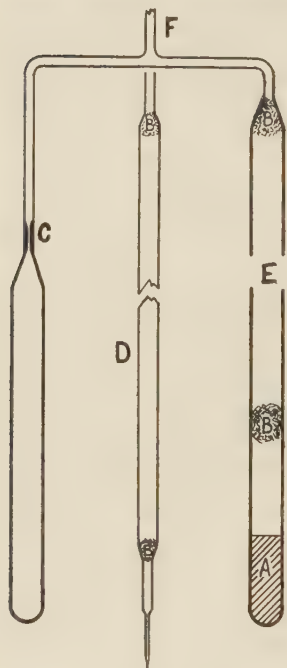


Fig. 3.—Apparatus used in drying and vacuum distillation of reaction mixtures. Pyrex glass used. A. Mixture of allyl bromide, hydrogen bromide and phosphorus pentoxide. B. Glass wool plugs. C. Piece of capillary tubing at which the receiver bomb tube is sealed off. D. Drying tube containing asbestos fiber and phosphorus pentoxide which is attached in this position when dried gases are to be admitted to the system after distillation. E. Bomb tube in which hydrogen bromide was dissolved in allyl bromide is sealed onto system at this point. F. Tube through which system is evacuated.

The required quantity (almost with exception, 10 g.) of allyl bromide was weighed out into the bomb tube shown at the right in Fig. 3. This tube was put into a freezing mixture at -75° and the necessary amount (10.0 g., 1.50 moles, except where noted) of dry hydrogen bromide gas was passed into the cold allyl bromide, care being taken to exclude moisture from the cooled tube. When the reaction was to be run in the presence of air, the bomb tube was simply sealed off at this point and put away. Otherwise the lower part of the bomb tube was immersed in liquid air, about a gram of phosphorus pentoxide was added, and a fairly tight-fitting glass wool plug was pushed into the tube as shown in Fig. 3. The rest of the apparatus shown was then sealed onto the top of this tube. The system was then evacuated to less than 3 mm. (often to less than 1 mm.), and at the same time all of the apparatus except that part of one bomb tube containing the reaction mixture was quickly heated with a hand torch to volatilize any moisture and gas that might be occluded on the inside walls. The connection to the pump was then sealed off without any gas entering the system. The contents were allowed to warm up to the temperature of a solid carbon dioxide freezing mixture, when they thawed out and were shaken gently with the phosphorus pentoxide for fifteen minutes or more at this temperature. The phosphorus pentoxide formed a finely dispersed, semi-gelatinous suspension in the liquid and settled only slowly after shaking.

The bomb tube containing the reaction mixture was then removed from the cooling bath and the other tube was put in so that the hydrogen bromide distilled over into the cooled bomb tube. The receiver was finally cooled in liquid air to bring over the allyl bromide. A vacuum distillation made in this way was fairly quiet, although bumping sometimes occurred with drying agents other than phosphorus pentoxide.

After the liquids were completely distilled off from the drying agent, which was not warmed at all, the receiver bomb tube was sealed off at the capillary tubing at its top. If capillary tubing were not used at this point, the seal sometimes blew in during sealing. Naturally, considerable pressures were developed when the bomb tubes reached room temperature, but the losses by explosion were less than 2%.

This technique seemed to meet quite well the necessary conditions imposed upon it. The apparatus had to be entirely of glass and without stopcocks, as lubricants and rubber might have contaminated the reaction mixtures. It was necessary also to dry the materials thoroughly and to remove them from the drying agent without any contact whatsoever with the atmosphere.

3. Method of Completing Determinations.—After the bomb tube had stood for the required time at the reaction temperature, it was cooled again in a solid carbon dioxide cooling mixture, opened by cracking with a hot wire at the top, and the contents were poured into a beaker of water. The product was then washed three times with water, dried with calcium chloride and distilled. Any high-boiling or polymerized products were eliminated by the distillation, but the quantities of these were always very small. The index of refraction of the distillate was then taken for the determination of the yield. The yields are calculated on the assumption that the index of refraction of a mixture of the dibromides with allyl bromide is a linear function of composition. The error involved in this assumption is small, as may be seen from Fig. 2.

The unreacted allyl bromide was then removed by the following procedure. Five cc. each of absolute alcohol and dimethylaniline were added, the whole shaken, and then allowed to stand at room temperature from seventeen to twenty-four hours. The absolute alcohol was added because in the preliminary trials described in Table XVIII, the quaternary ammonium salt formed from allyl bromide and the amine crystallized out of solution. Alcohol prevented the separation of this material, and although its use was unnecessary, the practice was continued for the sake of uniformity of procedure. After standing the required time at room temperature, the mixture was washed with 6-*N* sulfuric acid three times, with saturated bicarbonate solution once, and with water twice. The remaining dibromides were then dried over calcium chloride and distilled. The index of refraction of the mixture was then taken, and the composition of the addition product determined directly.

4. Modifications for the Use of Solvents.—In those runs in which solvents were employed, 1.5 moles of solvent was generally used to one mole of allyl bromide. Because the rate of reaction was usually slower, probably partly because of dilution of the reacting substances, more than the usual 1.5 moles of hydrogen bromide was often used, added in the manner mentioned previously. The only exception to this procedure was in the case of glacial acetic acid, which froze out if cooled very strongly at first. This difficulty was easily avoided by cooling the mixture gradually, for most of the acetic acid was soluble in the rest of the mixture at low temperatures after enough hydrogen bromide had been added. When the reaction mixture was to be dried and distilled *in vacuo*, the acetic acid and other solvents boiling above 100° were put into the receiver bomb tube directly and were not distilled. The same is true of antioxidants and catalysts.

Those solvents which could be removed by washing from the reaction mixture at the completion of the reaction were removed in this way. Solvents which were insoluble in water and which could not be conveniently removed by washing were removed by frac-

tionation, for all of the solvents in this class which were used boiled below 100° , more than 40° below the lower-boiling of the addition products. For this separation a short fractionating column was used, and the distillate was rejected until the boiling point of the addition compound was nearly reached. The column was then allowed to drain completely and the residue was transferred to the miniature distilling flask always used, because too much material would have been lost in an attempt to distil all of the addition product through the column. After distillation, the residues were treated with dimethylaniline to remove remaining traces of allyl bromide and worked up thereafter according to the usual procedure.

5. Estimation of Composition of Addition Products by Boiling Points.—In many cases, comparison of the boiling range of an addition product with its index of refraction showed that the latter was in error, due to remaining traces of solvent or other added material, small amounts of by-products formed, or remaining traces of allyl bromide. Trouble from the last-named cause was encountered only when poor yields were obtained and insufficient dimethylaniline was used to remove the unchanged allyl bromide. On a few occasions, extremely warm and humid weather made accurate determination of refractive indices very difficult. In practically all cases, however, the error in index of refraction was small, less than one in the third decimal place, but this represents an error of about 26% in the composition of the addition product.

Toward the end of this work, a boiling point table was worked out very carefully, using as a basis runs made under the most favorable conditions where good yields were obtained. The construction of such a table was possible because the initial, final and some intermediate points of boiling ranges had been recorded for all of the distillations made. The use of such a table was valid because the same apparatus was always used for the distillations, because the latter were made at approximately equal rates with approximately equal quantities of material, because the table was based on mixtures of known composition, and because the difference between the boiling points of the two dibromopropanes was large, about 24° . Therefore our estimates of percentage composition are probably always accurate within 7 or 8%, and are usually within the limit of error involved in the determination of composition by index of refraction, $\pm 5\%$. Because our table is purely empirical and of little value with other apparatus, its publication is omitted.

6. Source of Allyl Bromide.—Part of the allyl bromide employed in our work was purchased from the Eastman Kodak Co. The remainder was made very conveniently by a method suggested by Dewael¹² for the preparation of allyl chloride. 1.1–1.2 moles of gaseous hydrogen bromide was dissolved in pure allyl alcohol at 0° in the presence of 1–2% of cuprous bromide. Yields of 90–95% were obtained after the mixture had stood for a few hours at room temperature or at 10° . Allyl bromide from either source was further purified by washing with cold water, drying with sodium sulfate at -75° and distillation through a 1.5 meter column. The constants obtained were: b. p. (752 mm.) 69.6° ; n_D^{20} 1.4693.

7. The Stability of Allyl Bromide and its Addition Products.—Bromine was added to allyl bromide under a variety of conditions to show that there was no shift in the position of the double bond. The addition was performed in ordinary diffused light in ligroin, glacial acetic acid, 87% aqueous acetic acid and carbon disulfide, and without any solvent, and also 15 cm. from a 500-watt incandescent projection lamp in the last two cases. The products were all quite pure 1,2,3-tribromopropane, identified by freezing point, boiling point, and index of refraction.

The stability of both addition products toward light was demonstrated by exposing small samples of each to the light of a 100-watt frosted lamp for twenty-one hours. No change in index of refraction was noted. In another experiment, one-half mole of hydro-

(12) Dewael, *Bull. soc. chim. Belg.*, **39**, 40 (1930).

gen bromide was added to a small quantity of propylene bromide; the mixture was sealed into a bomb tube with air, and kept about 10 cm. from the same lamp for four days. No change in index of refraction or boiling point of the propylene bromide was found. This experiment shows that 1,3-dibromopropane, the product formed by the addition in the presence of light and air, is not the result of rearrangement of 1,2-dibromopropane under the experimental conditions of addition.

Summary

1. Methods have been developed for the study of the addition of hydrogen bromide to allyl bromide under carefully controlled conditions, removing the unchanged allyl bromide from the addition products, and for determining the yield and composition of the addition products by indices of refraction.

2. It has been shown that in the absence of oxygen and peroxides, hydrogen bromide adds very slowly to allyl bromide to give 1,2-dibromopropane, and that in the presence of small amounts of oxygen or peroxides, the addition is very rapid and the product is 1,3-dibromopropane.

3. The use of antioxidants has been introduced to eliminate the effect of peroxides on the addition.

4. The effects of catalysts have been investigated.

5. It has been shown that solvents, temperature, and probably illumination have no effect on the direction of addition of hydrogen bromide except in so far as these factors influence the peroxide effect. However, they may have a pronounced effect on the velocity of addition.

6. Work is actively under way in this Laboratory to ascertain how extensively the findings recorded in this paper may apply to other unsaturated compounds as well as to conjugated systems.

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